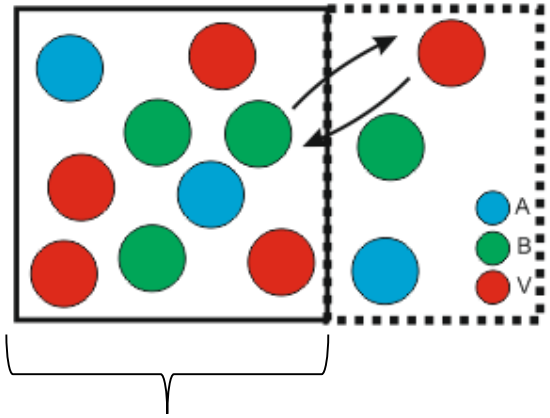
Erlangen 2019

Workshop

Exercise 1: Semi Grand Canonical Monte Carlo

System



Infinite reservoir

Number of particles N_{tot} (nodes) in the system is fixed

The system is in equilibrium with imaginary infinite reservoir of particles. For each element we introduce chemical potential, which governs the concentrations in the system. As the total number of particles is fixed, (N_{el}-1) relative chemical potentials Δ are needed for full description, where N_{el} is number of elements

$$\tilde{\Omega}(\{\Delta\mu_{pr}\}, N, T) \equiv F(T) - \sum_{p=1}^{n} \Delta\mu_{pr} N_p$$

SGC potential

F(T) ≡ Helmholtz free energy
N_p ≡ number of p-elements
$\Delta\mu_{pr} \equiv \mu_p - \mu_r$

Metropolis algorithm for SGCMC

1. Choose random lattice site *n*, occupied by element *p* (uniform)
2. Choose possible substituent *q* (uniform)
3. Calculate energy of substitution:

$$\Delta E = E(\Gamma_q) - E(\Gamma_p) + \Delta\mu_{pq}$$

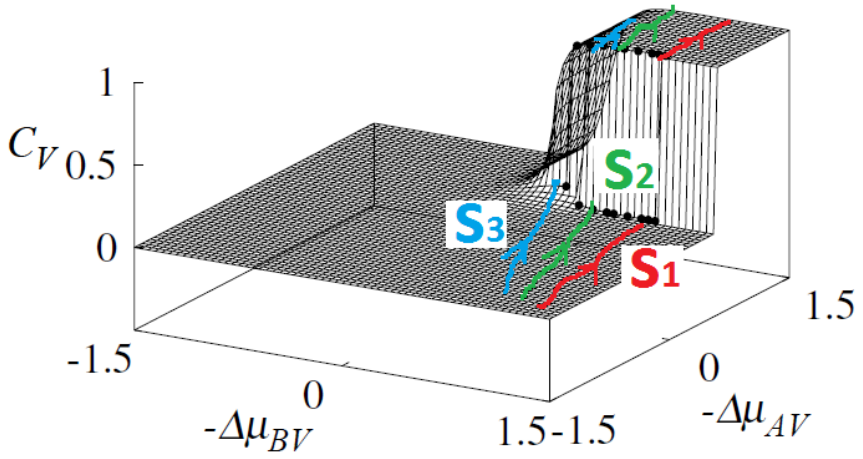
4. Calculate Metropolis probability for the substitution:

$$p_{pq} = \min[1, e^{-\Delta E/k_B T}]$$

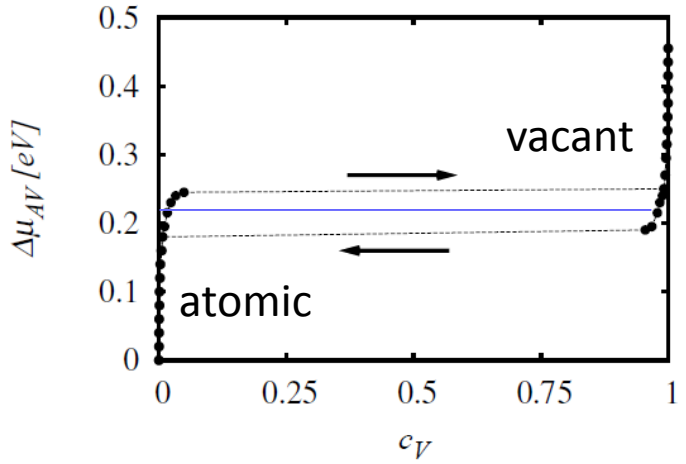
5. Generate random number $u \in (0,1]$
6. If $u \leq p_{pq}$ then accept substitution
7. Repeat steps 1-6, until system reaches equilibrium (energy saturates)

Exercise 2: Application of SGCMC - equilibrium

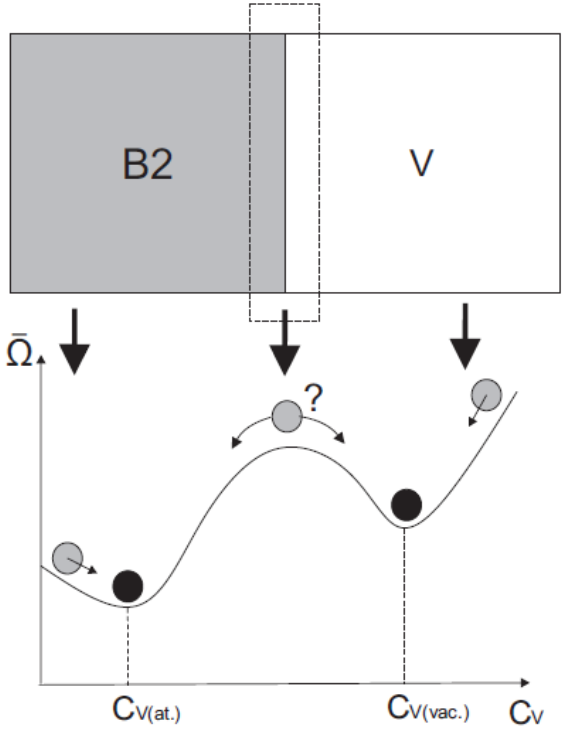
Stoichiometry paths



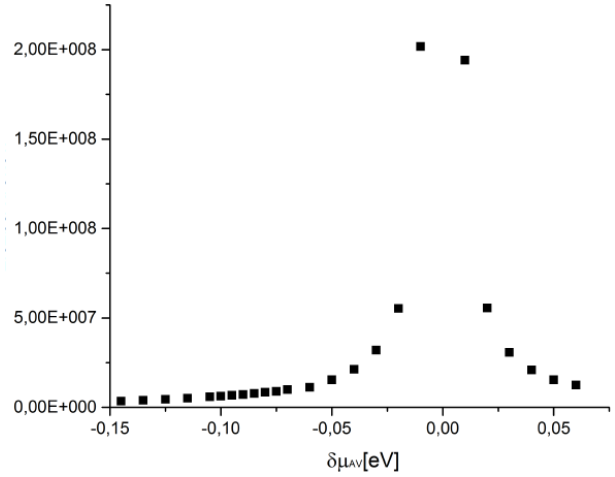
Hysteresis and equilibrium point



Coexistence of phases and driving force

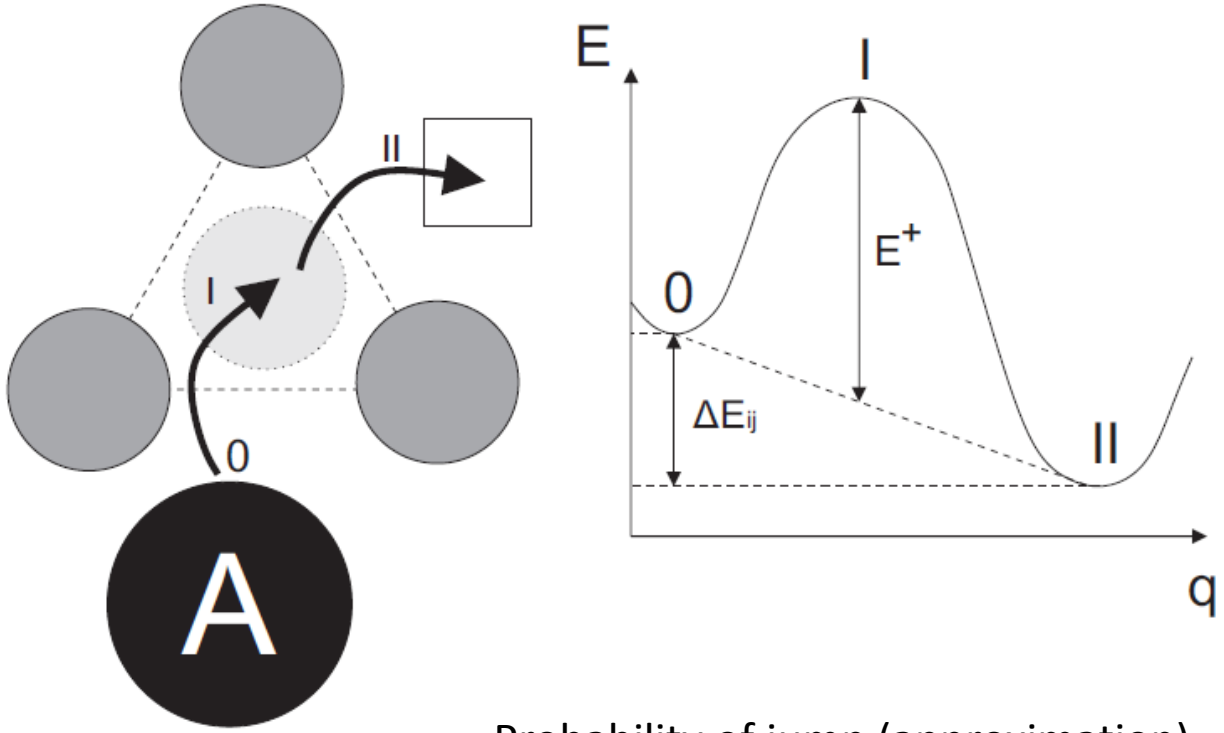


Time of homogenization



Exercise 3: Kinetic Monte Carlo and Diffusion

Atomic jump to vacancy and energy barrier



Probability of jump (approximation)

$$P_{ij} = e^{-\frac{E^{+} + \frac{1}{2}\Delta E_{ij}}{k_B T}}$$

Residence Time Algorithm for KMC:

1. Make catalogue of all possible transitions and its probabilities Pij for initial microstate σ_i
2. Normalize all transition probabilities by following term:

$$R = \sum_{j \neq i} P_{ij}$$

3. Project normalized probabilites on an unitary axis
4. Choose with uniform probability a number in range [0,1] and find segment (transition) to which it belongs. **Realize the transition.**
5. **Increase Monte Carlo time by:**

$$\Delta t = \frac{\tau}{R}$$

6. Repeat until the all relevant data is aquired with good statistics.

Exercise 3: Kinetic Monte Carlo and Diffusion

Direct Exchange (with Glauber probabilities)

Glauber probabilities of transition between microstates *m* and *n:*

$$W\left(\Gamma_m \rightarrow \Gamma_n\right) = \frac{1}{\tau}\frac{\exp\left(\frac{-\Delta E}{k_b T}\right)}{1+\exp\left(\frac{-\Delta E}{k_b T}\right)}$$

,where

W = frequency of transtion $\propto$ transition probability

τ = time constant

$\Delta E = E_n - E_m$